

Microstructural Changes in Coal During Low-temperature Ashing*

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Introduction

In the present work, the microstructural changes occurring in two U. S. coals during low temperature ashing (LTA) have been examined using a scanning transmission electron microscope (STEM) and automated image analysis in an electron microprobe. The latter, a computer based technique, can be used to provide a quantitative analysis, by species, of the mineral particles $>0.2 \mu\text{m}$ in diameter in petrographic samples of powdered coal. A full description of the operation of automated image analysis routines for coal science application may be found elsewhere(1-5). The STEM, by comparison, with its high spatial resolution for imaging and compositional analysis, can be used to examine ultra-fine mineral particles (diameters $<0.2 \mu\text{m}$) in coal(6-9), and also to directly determine the principal inorganic elements chemically bound in the organic coal matrix(9). These two techniques therefore can be used together in a complementary manner to provide a detailed characterization of the mineral matter in coal samples(9). For the present task, their ability to work directly on either raw coal or ash samples was also a great advantage.

In support of the electron optical analysis of LTA transformations, complex thermochemical calculations have also been made. These calculations serve two purposes. The first is to provide a more fundamental thermodynamic understanding of mineral matter behavior under LTA conditions. Secondly, the calculations assist the electron microscopist in identifying species by predicting the possible products of observed reactants. This serves as guide when it becomes necessary to distinguish various species by electron diffraction, rather than energy-dispersive X-ray spectrometry (as when dealing with the many oxides, sulfides, and sulfates of iron). The limitation on this computational technique is that chemical equilibrium is assumed but may not be reached over the duration of a typical LTA experiment.

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Experimental

The coals used in the present experiments were PSOC 98, a high-volatile-C bituminous coal from Wyoming (Bed #80 seam), and PSOC 279, a high-volatile-B bituminous coal from Indiana (Indiana #3 seam) obtained from the Penn State Coal Bank. The low temperature ashier used in the present work was an LTA-504 from LFE Corporation. During ashing, small specimens were removed from a sample of each coal after 1, 3, 6, 12, 24, 48, and 72 hours of ashing. These partially-ashed samples were used for subsequent STEM analyses.

Thermochemical Modeling

The complex equilibrium code used in this work was an extension of the code originally developed by Erickson(10-12) and later modified by Bessman(13). The code, SOLGASMIX-PV, has been interfaced with a data base that is a compilation of thermodynamic data from JANAF(14) and the U.S. Geological Survey(15).

The elements included in the equilibrium calculations were: H, C, O, Mg, Al, Si, S, Ca, and Fe. The numbers of moles of each element (based on the analyses of each coal) were entered as oxides. An excess of oxygen was included to simulate the oxygen-rich environment of the LTA. The equilibrium temperature was set at 150°C with a pressure of one atmosphere. The list of species investigated for equilibrium stability is too long to present here, but included all of the combinations of the above elements given in the JANAF data base as well as many carbonates, sulfates, alumino-silicates, and sodium-aluminum silicates tabulated by the U.S. Geological Survey.

Results

PSOC 98

Low temperature ashing produced radical structural changes in PSOC 98 which resulted in individual ash particles having a gauzy appearance in the STEM. Stereomicroscopic examination revealed that the "gauze" was a fine three-dimensional network with denser particles suspended within the ash matrix. STEM microanalysis showed these dense particles to be the same sort of mineral inclusions observed in the raw coal. Electron diffraction patterns taken of the ash showed crisp rings characteristic of crystalline material. Analysis of the ash matrix in the STEM revealed Ca and S, as in the raw coal matrix. With this additional compositional information, the diffraction patterns were indexed and the presence of the mineral bassanite, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, was established. The grain size of the bassanite networks forming the matrices of the ash particles was on the order of 30 nm, as determined from standard dark field images formed from portions of the bassanite ring pattern.

Subsequent X-ray diffraction analysis of the material ashed for 72 hours showed bassanite to be one of the three principal minerals found after LTA (together with quartz and kaolinite).

PSOC 279

The raw particles of PSOC 279 were similar in appearance to those of PSOC 98. The most commonly observed type of ash particle, however, consisted of an agglomeration of mineral particles, principally quartz, clays, and pyrite. These were the predominant mineral species found in the raw coal by the electron microprobe analysis. These were also the three major species found by X-ray diffraction in the material ashed for 72 hours.

"Gauzy" ash particles, very similar in appearance to those in the PSOC 98 ash, were less common than the agglomerate type but were also found in the STEM samples. The characteristic inorganic signature of the organic matrix of raw PSOC 279 particles was a combination of an Al and a Si signal. Again, the same combination was carried over into the matrices of the gauzy type or ash for this coal.

STEM examination of the low temperature ash of PSOC 279 showed that much of the pyrite in the starting coal survived the full 72 hours of ashing. This was confirmed by the X-ray diffraction analysis of the ash, as mentioned earlier. STEM analysis was also done on particles of small (<80 nm diameter) crystals. These particles were Fe and S rich, but with much lower S:Fe ratios than pyrite. A significant portion of these particles had a cubic morphology. No minerals of this type were observed during STEM examination of the raw Indiana coal.

Modeling Results

Figure 1 illustrates the stable condensed phases predicted by the equilibrium calculations for low temperature ashing conditions. The results shown are for PSOC 98 but apply as well for PSOC 279 except for the relative amounts of each specie.

Discussion

Bassanite formation is commonly observed during low temperature ashing, particularly for western coals. It is believed to form by three means: dehydration of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) found in the raw coal(16,17), reaction of organic S and the mineral calcite (CaCO_3)(18), and direct reaction of organic Ca and S(19,20). These reactions have proven to be hard to distinguish, because of the difficulty of analyzing the starting mineral content of raw coal samples by conventional techniques, and the inability of these same techniques to find and examine partially-ashed

particles to observe the reaction in progress. The use of the electron-optical analysis techniques described in this paper, however, overcame both of these problems, as will now be described.

The STEM results for PSOC 98 indicate that the organic matrix of the raw coal contained Ca and S in a non-crystalline form. This is consistent with the Penn State sulfur-forms analysis which indicates that most of the S in the coal is in an organic form. It also explains the relatively small percentages of Ca-bearing minerals found by the electron microprobe, since other information indicates that PSOC 98 contains a relatively large amount of calcium.

Apparently, the organic matrix of the coal itself was the origin of the Ca and S needed for bassanite formation. The fact that calcium sulphate would form under these conditions was confirmed by the results of the thermochemical calculations (see Fig. 1) which indicated that sufficient sulfur was present in the coal to react with the calcium and prevent the formation of other species, such as calcium carbonate (calcite).

The details of this LTA reaction process were brought to light by the STEM examination of the partially-ashed samples. In general, these samples were simply made up of mixtures of raw coal and fully-ashed particles in varying proportions, based on the amount of ashing time they had seen. However, it was still possible to find individual particles which themselves were only partially ashed.

In such a particle it appears that the fine bassanite network forms continuously as the organic material is burned away and the Ca and S are freed from the matrix. Mineral inclusions originally present in the raw coal particle often remain entrapped within this network as it forms. The bassanite network created thus determines the structure of the low temperature ash of PSOC 98.

It is interesting to speculate on the possible origin of the "gauze" developed by this reaction. It is well known that for coals from the western U.S., organic Ca is readily ion-exchangeable(21). This indicates that the Ca has ready access to the pore structure of the coal. If, during LTA, the Ca in the raw coal reacts in place with the organic S and the oxygen plasma, it could be that the bassanite gauze produced has a network structure related to the pore structure of the raw coal. The 30 nm size of the bassanite crystallites is also comparable to the diameters of a significant portion of the pores likely to be found in coal(22). It may therefore be possible to obtain heretofore unobtainable topographical information of the pore structure of pulverized coal particles by careful LTA experiments. This information would be of great use for modeling the combustion of such particles in commercial boilers. Further work is under way to investigate this possibility.

Although most of the ash produced from PSOC 279 consisted of particles

which appeared to be agglomerates of the mineral inclusions found in the raw coal, some "gauzy" particles were also generated during ashing. In analogy to the results from PSOC 98 just described, this suggests that the gauze was produced from inorganic elements chemically bound in the organic matrix of the starting coal. Unlike the Wyoming coal, however, the coal from Indiana had a matrix that contained primarily Al and Si. This combination of elements has been found by STEM analysis in the matrix of another midwestern coal as well(9). The STEM analysis of the gauzy ash particles for PSOC 279 also showed principally Al and Si. It appears that for this coal, the Al and Si from the organic matrix could react during ashing to produce new crystalline mineral matter. This transformation during LTA has not been previously reported.

The thermochemical modeling of the system indicated that Al and Si should preferentially react together with the oxygen of the LTA plasma to form one or more alumino-silicate compounds, as opposed to the separate formation of alumina and silica. This could not be directly confirmed by electron diffraction in the STEM, for several reasons. First, the mineral inclusion content of the gauzy particles was much higher for this coal than for PSOC 98. In addition, the microprobe results show that nearly 30 percent of these inclusions were alumino-silicates of various types. Selected area diffraction patterns of portions of gauzy particles therefore tended to be quite complex, and not readily amenable to interpretation. An attempt was made to use microdiffraction on the small regions of the network matrix which appeared to be relatively inclusion-free. However, the material was quickly destroyed by the high beam currents involved. The most that can be said from the present work is that STEM microanalysis supports the prediction of the thermochemical model by confirming the combined presence of Al and Si in the matrix of the gauzy ash particles from PSOC 279.

The thermochemical modeling also predicts another LTA transformation for PSOC 279. The modeling results indicate that pyrite is not a stable phase under the low temperature ashing conditions, and is expected to transform to an $\text{Fe}_2(\text{SO}_4)_3$ -type compound. Sulfur is expected to leave the system as SO_3 vapor.

A variety of LTA transformations involving Fe- and S-bearing compounds have been reported previously. Pyrite has been reported as either remaining unchanged(16,25), reacting to form coquimbite and other Fe^{3+} sulfates(17,24,25), or oxidizing to hematite(19). It is generally accepted that rozenite and other Fe^{2+} sulfates oxidize to Fe^{3+} sulfates during LTA(17,23-25). Indeed, in the most recent of these papers it was shown by Mossbauer spectroscopy that, for the LTA conditions used, all of the Fe^{3+} sulfate produced during LTA originated from the Fe^{2+} sulfate in the starting coal, while the pyrite remained unaffected(23).

The STEM results of the present work indicate that a significant amount of pyrite did appear to react during LTA. The pyrite that survived the LTA retains its dense appearance under STEM examination, along with its cubic morphology and high sulfur to iron ratio. By comparison, the

decomposition product has a highly porous structure, a much lower S:Fe ratio, and, in many (but not all) instances, has apparently lost its overall cubic shape. It was difficult to obtain electron diffraction patterns from these latter particles because of their unstable nature under the electron beam. In the few instances where a diffraction pattern was successfully recorded, the best fit for indexing the pattern appeared to be the Fe³⁺ sulfates, coquimbite and para-butlerite. The large proportion of these low S:Fe ratio particles (relative to surviving pyrite particles) observed in the ashed PSOC 279 rules out the possibility of their formation being completely the result of the oxidation of the starting iron sulfates in this coal. Only a very small fraction of the starting mineral matter in the coal was present in the form of Fe²⁺ sulfate.

For the LTA conditions used in the present work, pyrite in the starting coal did partially decompose. This appeared to occur on a particle-by-particle basis; no intermediate reaction products were observed. The rather sporadic nature of the decomposition of pyrite during LTA has been shown previously in tests where pyrites from different sources were subjected to LTA(19). The reason for this behavior is still not known.

One additional prediction of the thermochemical modeling requires comment. SiO₂ is not thermodynamically stable under LTA conditions, but instead should be reacting with other compounds to form aluminosilicates. However, silica particles were still easily identifiable as a species surviving LTA. There are at least two possible explanations for this. The first is that silica was generally found in relatively large particles, and so was not able to mix intimately with other compounds. Secondly, the kinetics of many reactions may be too slow for them to take place in the time frame of a LTA experiment. As was pointed out earlier, the thermodynamic models assume that equilibrium is reached.

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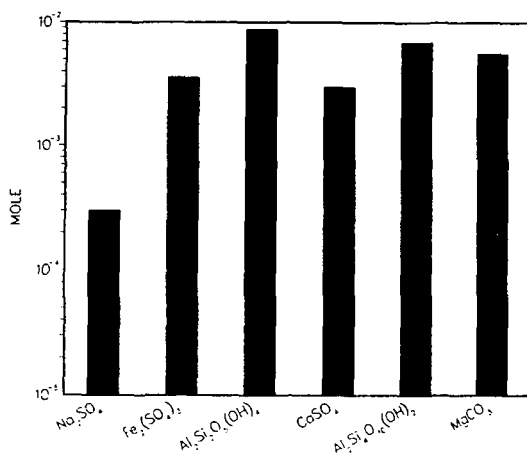


Figure 1 - Thermodynamically stable condensed phase species as predicted by the equilibrium thermochemical modeling. The plot shows the number of moles of each stable species that would be produced after equilibrium was reached under LTA conditions. The starting material was 100 g of PSOC 98.